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(54) Title: A METHOD FOR THE MANUFACTURE OF LIGHT-STABLE PAPER FROM MECHANICAL PULP, AND PAPER PRODUCED IN ACCORDANCE WITH THE METHOD

(57) Abstract

The invention relates to a method in which machine-finished paper or paper under manufacture in, e.g., a fourdrinier machine, is coated on both sides thereof with a protective coating containing materials or substances which will reflect ultraviolet light and also absorb such light. Provided on top of the protective coating is a pigment coating which contains luminescent materials, such that the remitted light will obtain a wavelength composition such that the human eye will discern the paper as preferably white.

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A method for the manufacture of light-stable paper from mechanical pulp, and paper produced in accordance with the method

The present invention relates to a method for improving the light-stability of paper, preferably paper produced from lignin-rich mechanical or thermomechanical pulps, so-called high yield pulps, and to paper produced in accordance with the method.

Those factors which are primarily influential in causing the poor light-stability of the high yield pulps, resulting in relatively rapid yellowing of the paper produced, are the lignin, extract and metal-ion content of the pulps. Lignin is considered to be the greatest contributory factor to yellowing of paper produced from such pulps, and consequently research has been concentrated on establishing those chemical and physical mechanisms which control the negative influence of lignin on the light-stability of paper.

Some of the first scientific works carried out on the basis of wood chemistry observations, in an attempt to describe the part played by lignin in the yellowing of paper produced from high yield pulps, were presented by Leary in the publications TAPPI 50 (1967):1, 17 and 51 (1968):6, 257. Leary discovered that irradiation of newsprint in a completely oxygen free atmosphere failed to result in yellowing of the paper. This confirmed the significance of oxygen on the yellowing of high yield pulps.

Other important contributions have been made by Kringstad and Lin and published in TAPPI 52 (1969):6, 1070; 53 (1970):4, 658; 53 (1970):9, 1675; 1 (1970), 252. They found that lignin compounds which contained ring-conjugated alpha carbonyl bonds, alpha-beta-olefin bonds or biphenyl bonds are sensitive to light-induced chemical reactions, resulting in yellow reaction products. On the other hand, those lignin structures whose side chains are saturated are resistant to radiation down to a wavelength of 300 nanometers.

Wood chemists believe that yellowing of paper is mainly caused by the phenolic components of the lignin present. It has been found that yellowing can be reduced significantly, by blocking these phenolic units, by acetylating or reducing the carbonyl and olefinic groups present in the lignin, with the aid of, inter alia, sodium borohydride. Other important steps include the reduction of certain aldehydic and quinone groups, e.g. benzoquinone groups, in order to counteract the formation of chromophores, i.e. the formation of substances capable of discolouring paper.

At the present time considerable background data is to be found concerning research into those mechanisms which control the yellowing of paper produced from mechanical pulps.

Since it is demonstrable that there are many reaction paths which lead to the formation of chromofore compounds, yellowing, when viewed chemically, is a highly complex problem. A quite expensive process technique and a relatively large input of chemicals would be required to achieve good colour stability (by implication whiteness) solely by chemical treatment, which renders such

treatment less attractive from an economic aspect and also from an environmental aspect.

Various methods have been applied in the paper industry with the intention of achieving maximum brightness in paper produced from high yield pulps. These methods include

1) the selection of high grade, white paper raw materials

2) treatment with chemicals (bleaching of raw materials)

3) mixing white filler and optical bleaches (whitening/-brightening agents) with the paper pulp, and

4) coating the paper with a high-grade coating substance that contains filler and an optical bleach.

Various methods have long been used in the paper industry to surface treat different kinds of low quality paper. The purpose of surface treatment is to improve the quality of the paper in one way or another, primarily its printability. Among other things, the brightness of the paper (often poor) and the light-stability thereof are also improved. This requires the application of a relatively thick coating, however.

Paper is normally surface treated with a coating composition containing a filler (often kaolin), a binder and various additives (auxiliary chemicals).

A wealth of paper coating compositions are described in the literature, inter alia in

- Coating formulations A.H. Nadelman, Lockwood Trade Journal, New York 1966

- Pulp and Paper, J.P. Calsey, vol. 3, Interscience Publ. 1961.

Coating substances or formulations are applied to paper in order to modify its surface properties, such as brightness, opacity, printability, mechanical strength, the paper's water retention, etc. The coating can be applied with the aid of rolls in a so-called paper coating section, or with the aid of doctors against special abutment rolls, or against drying cylinders in a fourdrinier machine. In addition to containing one or more fillers and one or more binders, a coating formulation may also contain an emulsifier, polysaccharides, dispersing agents, UV-absorbents, optical bleaches, foam retarders, fungicides, etc., as described in SE-B-7502846-4 (= FR-B-7408729). Other coating formulations are described in EP-A1-0015517, SE-B-.350083, SE-B-353358 and SE-B-7908927-2. The latter three publications relate primarily to grain size distribution.

In addition to the risks incurred by the introduction of a plurality of mutually different chemicals to a manufacturing process and the subsequent danger of spill, which may be impossible to take care of to a greater or lesser extent, the filler incorporated in such coating formulations must also be considered to constitute a contaminant. Furthermore, even though the binders used in the present context have relatively low vapour pressures at the working temperatures which prevail during paper manufacturing processes, the fact that binder vapours are present in the working environment of a paper mill cannot be ignored.

The contaminating character of fillers (pigments) is manifested at the present time when paper fibres are

recovered from recycled paper. Even though recycled paper constitutes the starting material for paperboard and for interlayers or for fluting, where, for instance, clay may be preferred, the filler will create disruptions in other uses of the paper fibres. Although the clay present can be held suspended to a large extent in the paper pulp, and therewith be prevented from forming deposits in the board or paper sheets produced, the clay will nevertheless create wear on pumps and valves in particular, during passage of the pulp to the paper machine. It should be remembered in this connection that the coating formulation constitutes up to 20% of the weight of the recycled paper, which creates problems unless other recycled fibres are available for admixture with thinning of the pulp. When manufacturing toilet and kitchen paper, which is produced totally from recycled paper, it is economically impossible to sort the recycled paper manually in an endeavour to limit the amount of coating formulation carried to the manufacturing process. The buffer volume of pulp sheets is the only auxiliary means for thinning out the coating formulation, if a given batch of recycled material has a high coated paper content.

In the case of paper of this kind, it is not believed that the filler present will constitute a problem in the end product. However, the risk of allergic reactions in the mucous membrane of those coming into contact with the paper concerned cannot be ignored, unless the recycled paper is cleansed of the binder present in the coating formulation, in several stages.

The object of the present invention is to provide a paper of sufficient quality for archival use and having

good print contrast made from relativ ly inexpensive starting material. The invention effectively reduces the load on the environment of hitherto used coating chemicals, which are mainly imported to paper producing countries.

By archival use is meant that the paper shall not subsequently yellow or be changed in any other way such as to reduce the contrast between paper and the text printed thereon or any other form of print or writing thereon, either when the paper is stored in a dark environment or when the paper is exposed to natural or artificial light. It shall be observed in this context that paper used in office copying machines is subjected to a relatively large quantity of luminous energy (light) therein. This light has a wavelength composition which ensures rapid transfer of text and images, but which is unkind to the paper fibres.

The desire which the invention is intended to fulfill is primarily is one of providing a paper which, over the passage of time, will remain white, as far as can be discerned by the human eye. When practising the novel method, however, it is also possible to manufacture paper which will be discerned by the eye as being slightly coloured in a pink, green, blue or some other hue. The natural tendency of the paper fibres to yellow is inhibited in all instances, and the paper surfaces will reflect light within the desired wavelength range.

For the purpose of reducing the use of chemicals and of improving the light-stability of paper produced from mechanical or thermomechanical pulp, it is proposed in accordance with the invention that the paper is treated in accordance with a method which, subsequent to speci-

fic chemical processing of the pulp against

- - - the phenolic units in the lignin present,

- - - conjugated alpha-carbonyl-structures (reduction)

- - - alpha-saturated and beta-saturated sidechains (hydration),

is characterized by the following process steps:

Applying at least two coating layers to the paper surface,

Coating 1 (nearest the surface of the paper), designated the protective layer, comprising an inorganic pigment which is both UV-reflective and UV-absorptive,

Coating 2 (external of layer 1) forming an outer layer having maximum brightness and comprises an optical bleach (whitening substance/brightener) and inorganic filler.

Further characteristic features of the invention are set forth in the following claims.

It has been found, surprisingly, that the brightness of paper manufactured from relatively dark mechanical pulps is improved markedly as a result of the proposed surface treatment of the paper. Paper thus treated also obtains a marked improvement in colour stability and is insensitive to both natural and artificial light.

Coating 1, which is applied directly onto the paper, is intended to protect the UV-sensitive compounds of the paper, so as to avoid undesirable photolytic reactions

between energy-rich UV-radiation and, e.g., lignin structures containing ring-conjugated alpha-carbonyl-bonds, alpha-beta-olefin-bonds or biphenyl-bonds.

The protective layer is applied in the form of a thin coating comprising a pigment mixture, binder, dispersing agent and water. The pigment mixture may comprise the following substances:
a/ highly pure titanium dioxide (TiO_2) having a grain size of 0.1-1.0 micron (preferably 0.3-0.6 micron)

b/ highly pure barium sulphate ($BaSO_4$), grain size 0.1-0.8 micron (preferably 0.1-0.3 micron).

c/ highly pure, amorphous silicon dioxide (SiO_2).

a/ functions as an UV-absorber, b/ and c/ function as UV-reflectors.

The mixing ratio, calculated in parts by weight is 1-3 TiO_2 + 4-8 $BaSo_4$ + 1-5 SiO_2, preferably 2 TiO_2 + 6 $BaSO_4$ + 3 SiO_2.

The coating weight, or grammage, is 0.2-0.8 g/m^2 (preferably 0.3-0.6 g/m^2).
Usable binders include styrene-acrylate latex, methyl cellulose or PEO (polyethylene oxide).

The preferred dispersing agent is TU (nonyl-phenol-ethylene-oxide).

The protective coating suspension is produced from:
10 kg pigment mixture (TiO_2 + $BaSO_4$ + SiO_2)
10-20 kg binder
0.1-0.2 kg dispersing agent

985 kg (max) water, which may have a hardness of max 3 dH^{o} and an iron content of max 0.02 ppm.

This protective coating suspension can be used on dry paper (less than 7% moisture). The suspension is prepared with the aid of dispersing apparatus and is held under agitation, or stirring, until it is used for application on the paper web, preferably by spraying on dry paper.

When the protective coating, or layer, is applied in a paper machine, when the paper web has reached a dryness of between 65 and 75%, the water content of the suspension is lowered beneath 900 kg when spraying and still lower when stroking or rolling the coating suspension on the paper.

Coating 2, is applied on top of the protective coating and comprises one or more white pigments, the whiteness of which is further amplified by adding one or more optical bleaches. The white pigment may comprise pure qualities of titanium dioxide, barium sulphate, calcium carbonate or aluminium silicate having a grain size smaller than 1.0 micron. One of the aforesaid substances, or a mixture of several of said substances, can be used in the pigment coating, depending on the final use of the paper. The optical bleach used comprises one or more moisture-resistant, fluorescent, inorganic materials, so-called luminescent materials. Substances which can be used to particular advantage in this context are blue-reflecting substances such as strontium pyrophosphates ($Sr_2P_2O_7$:Eu) or zinc sulphide (ZnS:Ag). The paper can be toned blue, by increasing the quantities of these substances. If a pink-reflecting paper surface is desired, yttrium oxide (Y_2O_3:Eu) or

magnesium fluorogermanate can be used. Barium-magnesium-aluminate and zinc-cadmium sulphide will provide a green-toned paper.

Figure 1 illustrates excitation and reflection spectra for a blue-colour producing luminescent material (optical bleach), namely zinc sulphide, and Figure 2 illustrates a corresponding emission spectrum.

The term luminescent materials as used here and in the following refers to powder-form, inorganic materials which are special chemical compounds having pronounced luminescence in a crystalline state, achieved subsequent to subjecting the materials to a separate annealing process. Light is generated by these substances as a result of the coaction of large groups of atoms or molecules, at times whole crystals, which are subjects for excitation energy absorption.

Inorganic luminescent materials do not constitute ideal crystals, but have the form of true or actual crystals with lattice disruptions. The energy level forms in these true crystals have the greatest significance in the production of luminescence.

The production of the luminescent materials is characterized by reactions in solid phase, which normally produce non-stoichiometric compositions of the basic material and additives of special doping substances, so-called activators. When these are incorporated in the crystal structure, activator centers (luminescence centers) are created in the form of dispersed activator ions, or ion groups, which are later responsible for the emission of light.

The luminescent materials can be excited by different types of radiation and emit light within different wavelength bands. The exciting radiation is often UV-radiation (ultra violet), or at times also short-wave, visible radiation. Certain luminescent substances may require excitation by photons of higher energy content, for instance X-ray radiation.

Knowledge of the absorption, excitation and emission spectra of the luminescent materials, and their powder characteristics, i.e. the particle or grain size distribution and particle form, is of fundamental significance when choosing luminescent materials for different areas of use. The light-stability of the luminescent material in a given system (field of use) is also a decisive parameter.

In order for a fluorescent material to be suitable for use as an optical bleach (whitening agent) in a paper coating formulation, the luminescent material must possess the following properties:

1. The excitation spectrum must lie within the wave length range of 350-420 nm in order for the luminescent material to be excited by incident light.

2. The emission spectrum must lie within the wave length range of 400-500 nm, preferably 430-470 nm, with a maximum spectral bandwidth of 40 nm ("blue emitter").

3. The luminescent material must be light-stable against incident radiation and long-term resistant against moisture and other components present in the coating formulation.

4. The maximum grain size distribution of the luminescent material shall lie between 1 and 5 micron, preferably between 1 and 3 micron.

Luminescent materials which fulfill these requirements satisfactorily include particular luminescent powder types of magnesium tungsten ($MgWO_4$:W) and zinc sulphide (ZnS:Ag) or (ZnS:Ag + $CoO.Al_2O_3$). In certain cases, the substances can be used advantageously in mixture, depending on the intended use of the paper.

Binders which can be used in the pigment coating include styrene acrylate latex, polyethylene oxide or some other water-soluble binder capable of imparting to the paper properties which are favourable for given areas of use, particularly with respect to reflected light. The binder and white pigment may not have strong absorption frequencies within the spectral range of 280-400 nm capable of disturbing excitation of the activator centra of the optical bleach. Moreover, the respective refraction indexes of the white pigment and the binder should differ from each other as far as possible, so as to obtain maximum coverage ability. The coverage ability of the pigment coating is directly proportional to the relative refraction index. This is defined by the formula

$$n_{rel} = \frac{n_p}{n_m}$$

n_p = pigment refraction index

n_m = refraction index for surrounding medium (binder).

In addition to the binder, the surrounding medium (m) may comprise other additives (filler, extender) which are optically less active than the pigment. This implies

a lower refraction index, accompanied by a higher value of the relative refraction index.

For the purpose of suppressing "yellow blemishes" in the surfaces of the paper, the coating formulation (coating 2) should comprise fine-grain pigment and optionally extender, i.e. pigment and extender having a grain size beneath 1.0 micron. This fine grain size will amplify remission in the blue wavelength range in comparison with remission in the yellow wavelength range. Since remission is the diffuse reflection of incident light, the eye will discern the remitted light as the colour possessed by the surface viewed. This is primarily due to the fact that the remission comprises non-parallel radiation. The colour impression obtained from the paper surface in question will remain the same, irrespective of the angle from which the paper is viewed, i.e. irrespective of the reflection angle of the incident light. The remission will increase with decreasing wavelength. Thus, the remission is greater for blue light than for red light, measured at a constant grain size of the pigment present in the surface of the paper. In the case of the present invention, this affords the advantage that the short-wave blue light, which is a complementary colour to yellow light, is reflected to a greater extent than other light. This amplifies the impression of a blue-white to white paper. The paper will therefore whiten with time, since the wood fibres lying beneath the protective coating will yellow slightly, despite the presence of said coating, and therewith complement the initial blue tone. The mixture of UV-absorptive and UV-reflective substances in the protective layer determine the balance points, inasmuch as these can be selected such that the reflected wave length of 185 nm is dominant. UV-light of this wave

length is much richer in energy than yellow light, and upon remission is able to extinguish part of the yellow remission.

It is important that good dispersion of the primary grains is achieved when preparing the coating formulation. Any re-agglomeration of the pigments present will impair the brightness and covering ability of the pulp, and result in an irregular paper surface, which is experienced as a mat surface. It is therefore necessary to use an effectively operating dispersion apparatus and the addition of auxiliary chemicals, i.e. surfactants.

Coating formulations comprising four mutually different compositions have been tested, these compositions being:

A. 60.0 kg $BaSO_4$
2.0 kg optical bleach (whitening agent) ($MgWO_4$: W)
5.0 kg styrene-acrylate latex (binder)
0.1 kg surfactant
32.98 kg water, max 3 dH^o ; iron content, max 0.02 ppm

B. 60.0 kg TiO_2 + $BaSO_4$ (1+1 parts by weight)
2.0 kg optical bleach (whitening agent) ($MgWO_4$: W)
5.0 kg styrene-acrylate latex
0.1 kg surfactant
32.9 kg water , max 3 dH^o; iron content max 0.02 ppm

C. 60.0 kg TiO_2 + $BaSO_4$ (1+1)
2.0 kg optical bleach (whitening agent) (ZnS:Ag)
5.0 kg styrene-acrylate latex
0.1 kg surfactant
32.9 kg water, max 3 dH^o; iron content, max 0.02 ppm

D. 60.0 kg ZnO
2.0 kg optical bleach (whitening agent) (ZnS:Ag)

5.0 kg styrene-acrylate latex
0.1 kg surfactant
32.9 kg water $_{\text{max 3 dH}^{o}}$; iron content max 0.02 ppm

Light measurements have been taken with a spectrophotometer in the wavelength range of 380-800 nm. The relative brightness of the paper has been calculated from measured spectral data in accordance with the method described in Journal of Colour and Appearance vol. 1 no 5 1972 page 341. Rapid ageing of the paper has been compared by the xenon-method. The results are shown in the following tables.

TABLE 1

Measuring sheet	Rel.brightness (%) initial	Rel.brightness (%) aged (xenon-test)	(%) difference
Newsprint untreated	63	59	-6.3
surface treated			
coating 1 (protective coating)	65	62	-4.6
coating 1 + coating 2, alt. A	84	81.5	- 3.0
coating 1 + coating 2 alt. B	86	84	-2.3
coating 1 + coating 2 alt. C	89	87	-2.2

coating weight: coating 1 = 0.3 g/m^2, coating 2 = 2.0 g/m^2

TABLE 2

Measuring sheet	Rel.brightness (%) initial	Rel. brightness (%) aged	(%) difference
55% groundwood pulp + 45% soft-wood pulp untreated	70	65	-7.8
surface treated coating 1 (protective coating)	72.5	69.5	-4.1
coating 1 + coating 2 alt.A	90	87.5	-2.8
coating 1 + coating 2 alt.B	91.5	89	-2.7
coating 1 + coating 2 alt. C	94	92	-2.1
coating 1 + coating 2 alt. D	91	89	-2.2

coating weight: coating 1 = 0.4 g/m^2, coating 2 = 1.5 g/m^2.

The tables clearly show that the protective coating improves the resistance of the paper to yellowing, but by applying coating formulation to a surface weight of 1.0 g/m^2 on the test sheets a paper is obtained which will practically never age, i.e. will resist yellowing and retain its brightness. The presence of the protective coating enables the pigment coating to be made much thinner than would otherwise be the case. Experiments with paper where solely the protective coating was applied showed that the paper becomes more resistant to yellowing with thicker protective coatings. However, when weighing together all of the factors concerned with the intended use of the paper it has been decided that an optimum combination for optimum qualities will consist of a very thin protective coating (0.3-0.4 g/m^2) and a thin pigment coating (1.0-2.0 g/m^2). In the case of gravure paper, it is proposed that the paper is coated with up to 4.0 g/m^2 pigment in the paper machine followed by supercalendering.

The inventive method can be practised in two ways. In the first of these the protective coating is sprayed onto the paper web in a paper machine when said web has a dry solids content of between 65 and 70%. The paper is then dried in an intermediate step to a dry solids content of between 80 and 90%, whereafter the pigment coating is applied to both sides of the paper web, with the aid of a coating applicator or a doctor blade. When practising the alternative coating procedure, the paper is delivered from a paper machine to a separate coating machine, in which the protective coating is applied, either by spraying or with the aid of a doctor blade.

The protective coating is then dried and the pigment coating subsequently applied, either with the aid of rolls or with the aid of doctor blades. The coated paper is then finally dried, prior to being rolled-up or cut into lengths.

CLAIMS

1. A method for producing light-stable paper from mechanical or thermomechanical pulp, characterized by coating both sides of a paper web with a coating (protective coating) effective in obstructing primarily UV-radiation, and by applying a coating of known pigment on said protective coating.

2. A method according to Claim 1, characterized by applying the protective coating on said paper web in the form of an aqueous suspension containing 5-3 parts titanium dioxide, 4-8 parts barium sulphate, 1-5 parts silicone dioxide, binder and dispersing agent.

3. A method according to Claim 1 or 2, characterized by applying the protective coating suspension onto both sides of the paper web to a resultant dry solids content of 0.2-0,8 g/m^2, preferably 0.3-0,6 g/m^2.

4. A method according to Claim 1, characterized by admixing the pigment coating with fluorescent, inorganic material, so-called luminescent materials.

5. A method according to Claim 4, characterized by selecting the luminescent materials incorporated in the pigment coating from the groups magnesium sulphide, tungsten sulphide and zinc sulphide.

6. A method according to any one of the preceding claims, characterized by including in the pigment coating, in addition to luminescent materials, a substance or a mixture of substances from the following group of substances: titanium dioxide, barium sulphate, calcium

carbonate and aluminium silicate.

7. A method according to any one of the preceding claims, characterized by applying the pigment coating onto the paper web in the form of an aqueous suspension containing a binder, to a resultant dry solids content of 0.3-4.0 g/m^2, preferably 1.0-2.0 g/m^2, using a roll coating mill herefor.

8. A method according to any one of the preceding claims, characterized by spraying the protective coating onto the paper web subsequent to said web having passed a first calender and having a dry solids content above 65%; by applying the pigment coating to the paper web when said web has obtained a dry solids content of about 85%; and by subsequently passing the paper web through a second calender.

9. A method according to any one of claims 1-7, characterized by practising said method on dry, smooth paper (92-93% dry solids content), which is first sprayed with a protective coating, and then dried in an intermediate stage and coated with a pigment coating suspension with the aid of a doctor blade and then finally dried.

10. A wood-fibrous paper produced primarily in accordance with the method of Claim 1, characterized in that both sides of the paper are coated with an UV-radiation absorbing and reflecting protective coating on top of which there is provided a pigment coating which contains inorganic, fluorescent materials.

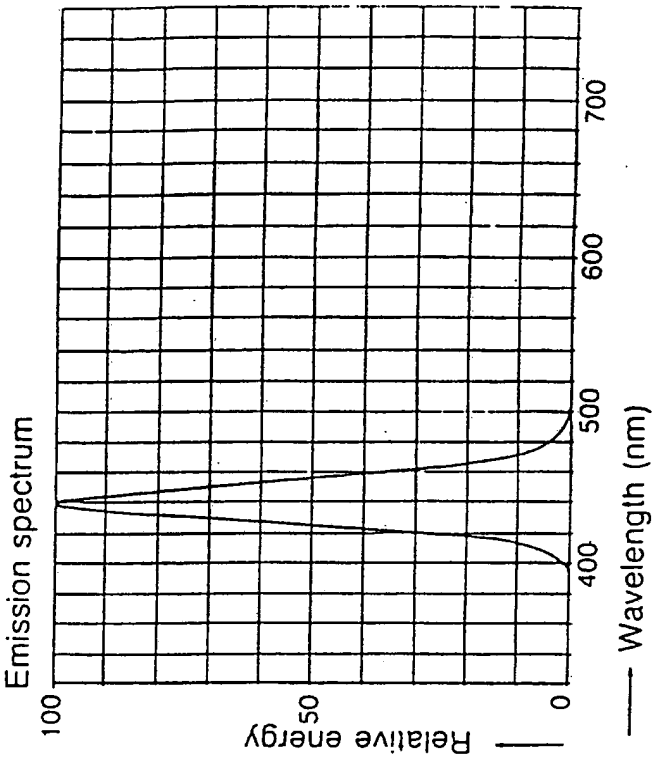
Emission spectrum
Relative energy
100
50
0
400
500
600
700
Wavelength (nm)

FIG. 2

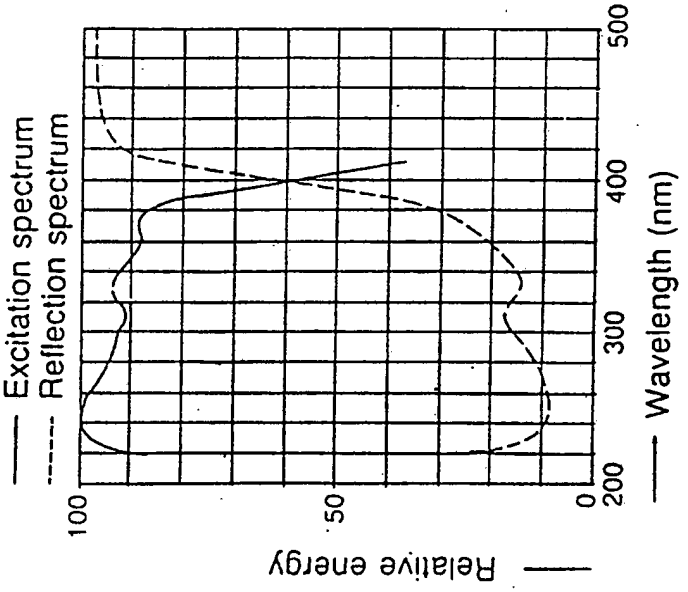
Excitation spectrum
Reflection spectrum
Relative energy
100
50
0
200
300
400
500
Wavelength (nm)

FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE89/00419

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC 4

D 21 H 1/22

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC 4	D 21 H
US Cl	162

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	SE, A, 7414268-8 (SVENSKA TRÄFORSKNINGSINSTITUTET) 13 May 1976 see the whole document	1
Y	SE, B, 310 599 (TIME INCORPORATED) 5 May 1969 see the whole document	1

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1989-10-26	1989 -10- 27
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